

**Phase Speciation Using Principal Component Analysis of EXAFS Spectra**

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Beamline(s) X16C

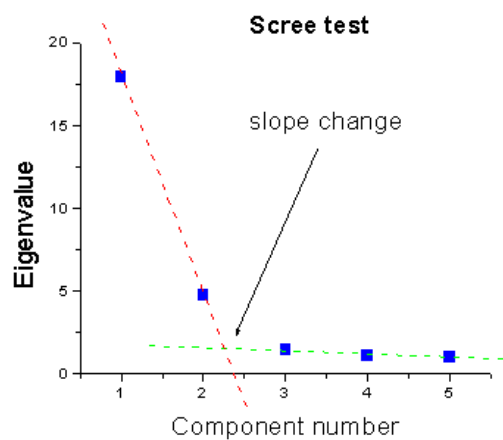
**Introduction:** The power of EXAFS spectroscopy as a quantitative structural technique has been limited, at large, by its application to the microscopically *homogeneous* systems where the local environment around each absorbing atom in the sample is the same. The growing interest in time-resolved EXAFS studies of chemical or biological systems has re-introduced the requirement for an analytical tool to probe *heterogeneous* mixtures generated by a catalytic reaction in real time. Conventional model-dependent fitting analysis is often ambiguous in these complicated systems. We report a new strategy to study mixtures by EXAFS using the principal component analysis. The test study of the five mixtures of two organometallic compounds illustrates the PCA method.

**Methods and Materials:** Cobalt acetylacetonate (Co-ACAC) and Cobalt tetraphenyl-prophine (Co-TPP) in analytical grade were purchased from Sigma. Five mixtures of  $[\text{Co-ACAC}]_{1-x}[\text{Co-TPP}]_x$  were prepared by mixing, with  $x=0, 0.33, 0.5, 0.67$  and  $1.0$ . The accuracy of the mixing was  $\sim 5\%$ .

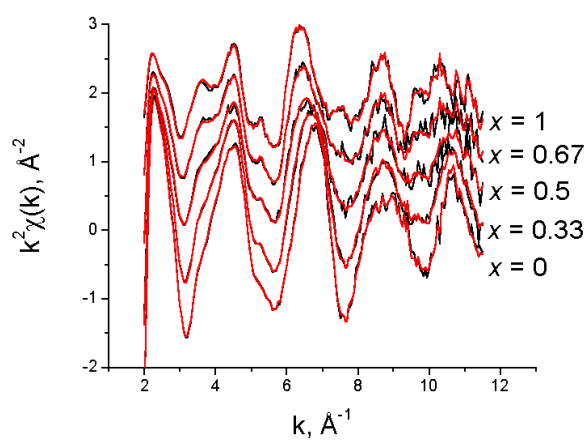
**Results:** The local structural environments in the Co-ACAC and Co-TPP pure compounds are dramatically different. In Co-ACAC the Co(III) ion is coordinated by six oxygen atoms at  $1.88 \text{ \AA}$  forming a distorted octahedron while in Co-TPP, the Co(II) ion is surrounded by four nitrogen atoms at  $1.95 \text{ \AA}$  in quasi-planar geometry. In this work, we have used the PCA method to analyze the EXAFS data of the mixtures. For all the five samples we obtained the set of five eigenvalues and eigenvectors (components). By examining the decay of the eigenvalues with the component number one can obtain the number of principal components (species in the sample) using the "scree test". The eigenvalues are plotted in the sequence of their decrease and the number of principal components is chosen where the curve levels off to a linear decline. Fig. 1 suggests a two-component mixture, since the eigenvalues level off beginning with the third component. The reproduction of the data using the two principal components is shown in Fig. 2. By a *linear* fit to the reference pure compounds, two of them, Co-ACAC and Co-TPP, provided excellent fit as expected. This proves that the two pure compounds indeed serve as good standards for this problem. After rotating the matrix of the components onto the matrix of the standard compounds data, the mixing fractions were obtained to be within 10-15% from the original compositions of all the mixtures.

**Conclusions:** The principal component analysis can be used to solve the phase speciation problem of the multi-component mixtures using their EXAFS data. The unique advantage of this method is its robust, model-independent determination of the number of unique species in the samples. If good experimental standards exist to represent each species, this method can also reliably obtain both the identities and the mixing fractions of all the species in the sample. This technique will be a powerful analytical tool for time-resolved XAS studies of biological systems.

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**Figure 1.** The eigenvalues level off beginning with the third component, indicating the 2-phase mixture



**Figure 2.** The raw EXAFS data (black) and their reproduction using the linear combination of two principal components